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(56) Documents Cited

None

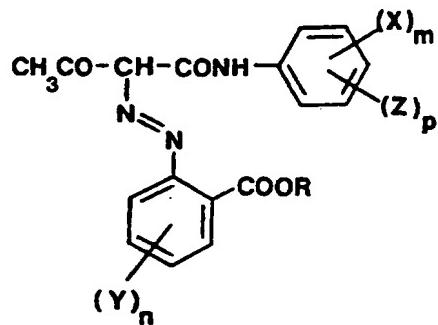
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Online: CAS ONLINE

(54) Abstract Title

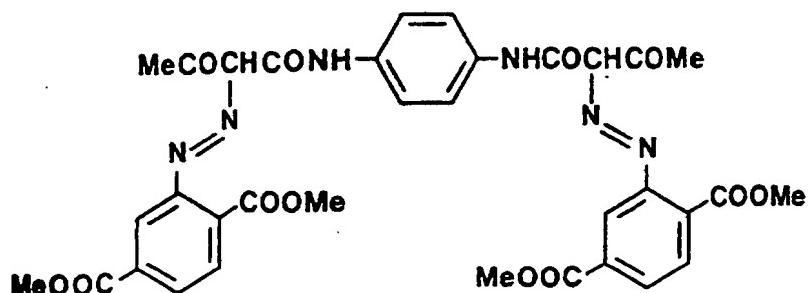
**Mono-azo compounds derived from diazotised 2-alkoxycarbonylanilines & N-[carboxy/sulpho]-phenyl] acetoacetamides and their use in pigment & ink compositions**

(57) There is provided an azo compound of formula I:-



[in which the group R is a lower alkyl group; (a solubilising group) is a sulphonate or carboxylic acid group or salt thereof; Y and Z are a lower alkyl group, a halogen, a group OR<sup>1</sup>, or a group COOR<sup>1</sup> (where R<sup>1</sup> is a lower alkyl group); m is 1, 2, or 3; n is 1, 2, or 3; and p is 0, 1, or 2; and lower alkyl group means an alkyl group comprising up to four carbon atoms].

There is also provided both a pigment composition and an aqueous ink which comprise a combination of a yellow or orange pigment and a compound of formula I. Preferably the yellow pigment is CI Pigment Yellow 155, of formula II :-



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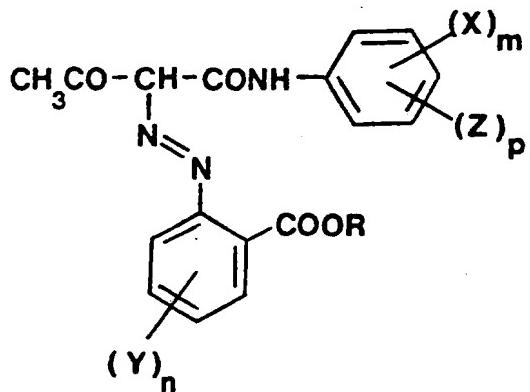
This invention relates to novel chemical compounds and to the use thereof for improving the dispersion properties of pigment compositions. More particularly it relates to the use for improving the dispersion properties of aqueous compositions comprising yellow or orange pigments and to the use thereof in inks.

Pigments are colorants which are effectively insoluble in the application medium. Various classes of Pigment are classified in the Colour Index International, published by the Society of Dyers and Colorists in 1997, and there are of course many other insoluble colorants which are not in this list. It is common practice to provide pigment compositions in the form of finely divided dispersions, which may be produced by many well known methods such as ball milling or by the methods disclosed in United States Patents 5026427 and 5310778. In order to obtain the optimum dispersion properties it is common to have present at least one dispersant or surfactant, and it is well known that the properties achieved by a pigment composition are crucially dependant on the dispersant used. The purpose of the dispersant is to stabilise the particles as they are formed, and to prevent particle growth by aggregation or flocculation. The dispersant or dispersants may be incorporated into the pigment at synthesis, may be added before or during the dispersion stage, may be added to the final dispersion or formulation, or may be added in a combination of these ways. Suitable dispersants are well known, and include, for example, polymers such as styrene/acrylic acid and styrene/maleic acid copolymers, surfactants such as alkyl phenol ethoxylates, and coloured compounds such as dyes which are structurally related to the pigment in use. For instance the use of salts of phthalocyanine sulphonic acids to inhibit flocculation of phthalocyanine pigment preparations is disclosed by United States Patent 2816045, United States Patent 3386843 discloses sulphonated quinacridone compounds and their use for improving the properties of

compositions comprising structurally related quinacridone pigments, and European Patent Application 451094 and Japanese Patent Application 63 178169 disclose sulphonated azo compounds and the use thereof in combination with related benzidine type yellow pigments.

We have discovered a new class of yellow azo dye which is useful for improving the properties of dispersions comprising certain high performance pigments such as those disclosed in German Patentschriften 1150165, 1544453, and 2103765, in German Offenlegungsschriften 2158806, and in United States Patent specifications 3997521, 4003886, and 4070353. This class of pigment has excellent performance, but there is a need to achieve the optimum properties from dispersions comprising such pigments as it can be difficult to achieve an adequately fine particle size without problems of aggregation or flocculation, and formulations may be subject to settling out.

Therefore according to the present invention there is provided a compound of general structure I:-



In which the group R is a lower alkyl group, X is a solubilising group which is a sulphonic or carboxylic acid group or salt thereof, Y is a lower alkyl group, a halogen, a group OR<sup>1</sup>, or a group COOR<sup>1</sup> where R<sup>1</sup> is a lower alkyl group, Z is a lower alkyl group, a halogen, a group OR<sup>1</sup>, or a group COOR<sup>1</sup> where R<sup>1</sup> has the meaning defined above, m is 1, 2, or 3, n is 1, 2, or 3, and p is 0, 1, or 2. By lower alkyl group is meant an alkyl group comprising up to four carbon atoms. Preferably the lower alkyl group is ethyl or methyl, and most preferably it is methyl. Preferably the group Y is COOMe and n is 1. Preferably p is 0. When the group X is the salt of a carboxylic or sulphonic acid then the counterion may be an alkali metal cation such as lithium, sodium, or potassium, an ammonium cation, a substituted ammonium cation such as triethanolammonium, triethylammonium, or pyridinium, or an alkaline earth or other metallic cation.

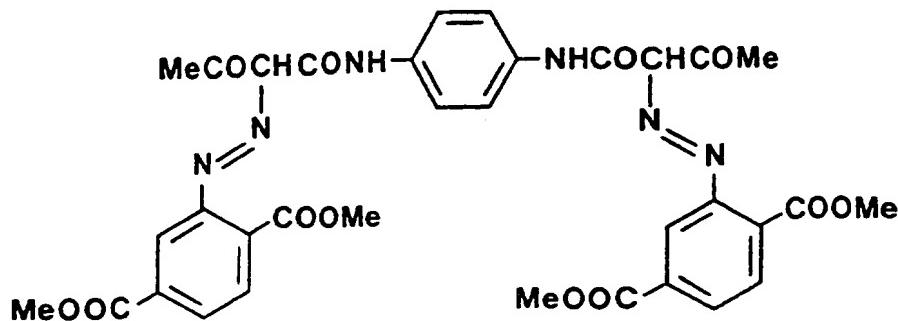
Specific useful compounds of formula I include the following:

COMPOUND	R	X <sub>m</sub>	Y <sub>n</sub>	Z <sub>p</sub>
A	Me	4-SO <sub>3</sub> Na	5-COOMe	H
B	Me	3-SO <sub>3</sub> Na	5-COOMe	H
C	Me	4-COOH	5-COOMe	H
D	Me	2-COOH, 5-COONa	5-COOMe	H
E	Me	2,5-(SO <sub>3</sub> Na) <sub>2</sub>	5-COOMe	H
F	Me	2-SO <sub>3</sub> Na	5-COOMe	H

Compounds of Formula I may be prepared by well known methods, and in particular by the standard synthetic method for azo dyes wherein a suitable amine is diazotised and coupled with the appropriate acetoacetamide. It is to be understood that the compounds of formula I are potentially tautomeric and may exist partly or completely in the alternative keto-hydrazone tautomer as is known for certain azo compounds.

The compounds of the invention are useful for improving the dispersion properties of pigment compositions comprising certain yellow and orange disazo pigments such as those disclosed by German Patentschriften 1150165, 1544453, and 2103765, German Offenlegungsschriften 2158806 and 2312421, and United States Patent specifications 3997521, 4003886, and 4070353. They are particularly useful for improving the dispersion properties of the disazo pigments of United States Patents 3997521 and 4003886. Therefore according to a second aspect of the invention there is provided a pigment preparation which comprises a combination of a yellow or orange pigment and a compound of formula I. Preferably the compound of formula I is in the salt form.

It is particularly preferred according to this aspect of the invention that the pigment is the compound shown as formula 20 of USP 3997521 and formula 2 of USP 4003886. This pigment is catalogued as Pigment Yellow 155 by the Colour Index and has the structure II below.



It is to be understood that the structure for the compound of formula II is shown as the conventional azo tautomer, but that the pigment may exist in the alternative keto-hydrazone form as is generally the case for yellow azo pigments (see for example the article by K.Hunger in Review of Progress in Coloration, volume 29, 1999 page 74).

Therefore according to this second aspect there is provided a combination of the pigment of formula II with the compound of formula I. According to this aspect the proportion of compound of formula I in the mixture is up to 100% by weight on the pigment, but preferably between about 1% and about 25%, and most preferably between about 1% and about 10% by weight on the pigment.

The compound of formula I may be added to the pigment at synthesis, as disclosed for example in United States Patent 5 151 129, or alternatively the compound of formula I and the pigment may be cosynthesised by a suitable mixed coupling reaction as is known in the art.

It is common practice to provide pigment compositions in the form of finely divided dispersions in a suitable carrier or solvent, which may be produced by a dispersion stage subsequent to the synthesis of the pigment. Therefore according to this aspect of the invention there is provided a pigment dispersion which comprises a combination of a yellow pigment and a compound of formula I dispersed in an aqueous solvent. Preferably according to this aspect there is provided a combination of the pigment of formula II with the compound of formula I. By aqueous solvent is meant a solvent wherein the liquid phase is predominantly water, but which may also comprise in addition at least one water soluble organic cosolvent.

According to this aspect it is preferred that the compound of formula I be added to the pigment at the dispersion stage. There may also be present in the dispersion at least one additional dispersant or surfactant. This additional dispersant or surfactant may be added to the pigment at synthesis, may be added as a grinding aid at the dispersion stage, or may be added after the dispersion stage. Suitable additional dispersants may include any of the dispersant types known in the art, but preferably the additional dispersant is a nonionic dispersant.

A suitable concentration for the pigment in a dispersion is up to about 50% depending on the dispersing method and the end use. A concentration of about 20 to about 25% is most suitable. If an additional dispersant is used then this may be present at up to 100% by weight on the pigment, but is preferably present at up to about 50% by weight on pigment.

According to another aspect of the invention there is provided an aqueous ink which comprises a combination of a yellow pigment and a compound of formula I. Preferably according to this aspect there is provided a combination of the pigment of formula II with the compound of formula I. By aqueous ink is meant an ink wherein the liquid phase is predominantly water, but which may also comprise at least one additional water soluble organic cosolvent. The ink compositions of the invention may also contain other components which are advantageously added to aqueous inks, such as surfactants, viscosity modifiers, biocides, and metal sequestering agents. Such additional components are well known in the art.

The aqueous ink compositions of the invention are especially suited to use in ink jet printers.

According to this aspect it is preferred that there is at least one organic cosolvent present in the ink, and most preferred that there is a combination of cosolvents present in the ink.

Suitable cosolvents are well known in the art, and include lower aliphatic alcohols and ketones, glycols and polyhydric alcohols, glycol ethers, heterocycles such as dioxan or tetrahydrofuran, nitrogen containing compounds such as urea, pyrrolidone, and alkyl pyrrolidones, and sulphur containing compounds such as sulpholane and thiodiglycol.

For this use, the concentration of the pigment composition in the ink is preferably between about 1% and 8% and the concentration of organic cosolvents in the ink is preferably between about 10% and about 50%, and most preferably between about 15% and about 25%. It is preferred to prepare inks by dispersing the pigment in the presence of the compound of formula 1 in deionised water to provide a dispersion, and then to dilute this dispersion to form the ink by adding additional water together with the organic cosolvents and any other additives.

The following examples will serve to illustrate the invention.

### Synthesis Example 1 - synthesis of compound A

Dimethyl aminoterephthalate (3.13g ; 15 mmol) in water (4ml), glacial acetic acid (8ml) and 30% hydrochloric acid (9ml) was stirred in an ice-salt bath. To this mixture was added a solution of sodium nitrite (1.05g ; 15.2 mmol) in water (20 ml) at such a rate so as to keep the internal temperature below 5°. The brown solution was stirred in ice for a further 30 min. The diazonium salt solution was then added dropwise during 20 min to a briskly stirred, chilled solution of p-acetoacetamidobenzenesulphonic acid sodium salt (4.04g ; 14.5 mmol), (Reference: British Patent 689,977), sodium hydroxide (1.25g ; 30 mmol), and anhydrous sodium acetate (2.04 g ; 25 mmol) in water (90 ml). A light yellow solid was deposited. The mixture was stirred at room temperature for 90 min, then heated at 95-100° (oil bath temperature) during 30 min. A yellow-brown solution formed, methanol (25 ml) was added; stirred at room temperature for 90 min, then in the refrigerator for 45 min. The mixture was filtered, washed ( little ice-cold water ; acetone ) and dried *in vacuo* at 60° to give a yellow solid 4.71g.

This material was heated under reflux in a mixture of tetrahydofuran (150ml) and water (15ml) for 1h, filtered, washed with a little ice-cold water and then acetone, and dried *in vacuo* over phosphorus pentoxide to yield a yellow solid 3.53g. (47%), Mp 329-331° (dec)

$$\lambda_{\text{max}} (\text{H}_2\text{O}) = 374 \text{ nm.}$$

$\text{C}_{20}\text{H}_{18}\text{N}_3\text{NaO}_9\text{S}\cdot\text{H}_2\text{O}$  Requires: C = 46.4%, H = 3.9%, N = 8.1%, Na = 4.4%. Found C = 46.1%, H = 4.0%, N = 8.2%, Na = 4.7%.

The following additional compounds were prepared similarly:-

Compound	Melting point
B	309 - 316° (dec)
C	294 - 295° (dec)
D	298 - 299° (dec)
F	324 - 325° (dec)

### Testing Example

#### Preparation of Dispersion

Compound A (0.15g) was dissolved in water (90g) using a magnetic stirrer, and a commercial (RTM) sample of Pigment Yellow 155 (10g) (available under the trade name Novoperm/Yellow 4G) was added while stirring. Once this had wetted out the composition was transferred to a Silverson mixer and mixed for 10minutes while the dispersing properties were observed. After a further 10minutes mixing the composition was transferred to a M110-F Microfluidiser and dispersed for 10minutes at 13000psi. Oversize particles were then removed by centrifugation at 3000rpm for 20 minutes to provide the final dispersion. This is dispersion 1 and it was compared with the comparison dispersion 2 prepared using the commercially available dispersant Sodium N-lauroyl sarcosinate and two control dispersions prepared as follows:-

DISPERSION	Addition	Observation
1 above (invention)	0.15g Compound A	Wetted and dispersed well
2 (comparison)	1g Sodium Lauroyl Sarcosinate	Wetted and dispersed well
3 (control)	Potassium p-Toluene Sulphonate	Thickened uncontrollably
4 (control)	None	Did not wet or disperse

Inks were prepared from these dispersions by taking 17.5g of the dispersion and letting down to 50g by adding a mixture comprising by weight urea (5%), thioglycol (10%), polyethylene glycol 300 (10%), and water (75%). The average particle size of the dispersions and of the inks was determined using a Polymer Laboratories Light Scattering Photometer.

The results are given below:-

Reference	Particle size of dispersion	Particle size of ink
1 (invention)	170nm	172nm
2 (comparison)	177nm	183nm

It is seen that the inventive compound A provided a somewhat smaller measured particle size than the comparison commercial dispersant despite being used at a lower concentration. Both dispersions could be formulated into inks without any significant increase in the measured particle size, showing that the dispersions are robust to the shock of the change of solvent at let down.

### Stability

The stability of the dispersions and inks was assessed by taking 5g samples in small sealed plastic tubes and storing in a water bath at 70° for four weeks. They were regularly inspected for evidence of instability such as flocculation or settling. None of the dispersions or inks showed any sign of settling out during this period, and both were judged to show excellent stability.

Samples of the inks were stored at room temperature for one month, care being taken not to allow any agitation. The samples were inspected weekly for any evidence of settling out. At the end of four weeks there was some slight settling of the ink 2 prepared using the control dispersant, but no evidence of any settling in the ink 1 prepared using compound A.

### Printing Performance

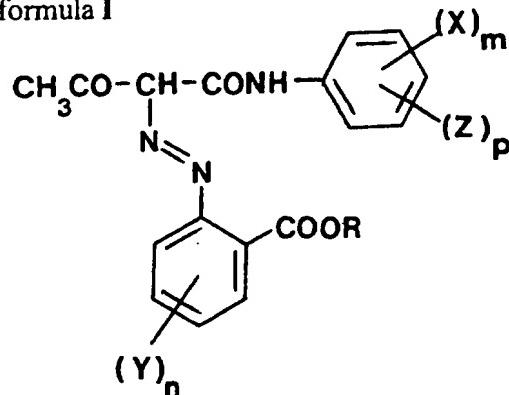
An HP51626a ink cartridge was filled with the inventive ink 1 and placed in an HP400 desk top printer. A solid fill test pattern was printed. The ink printed successfully immediately and gave a print showing an excellent and uniform fill of colour.

### Decap Performance

The decap performance of the ink was evaluated by leaving the filled ink cartridge uncapped for periods of one and five days, and then printing another test pattern. The cartridge fired up immediately on both occasions showing that the inventive ink has excellent decap performance.

Claims

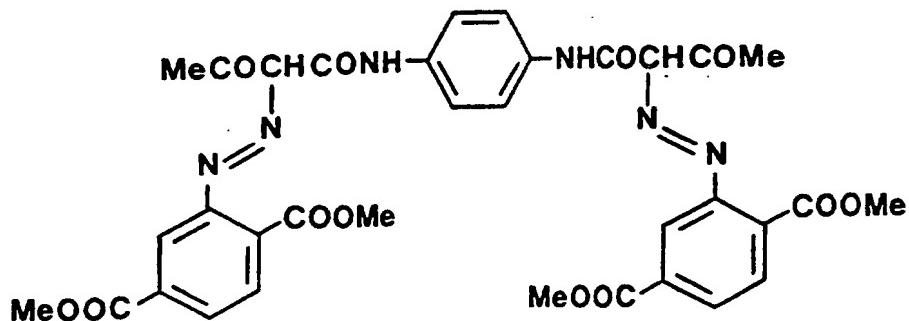
1. A compound of general formula I



In which the group R is a lower alkyl group, X is a solubilising group which is a sulphonic or carboxylic acid group or salt thereof, Y is a lower alkyl group comprising up to four carbon atoms, a halogen, a group  $\text{OR}^1$ , or a group  $\text{COOR}^1$  where  $R^1$  is a lower alkyl group as defined above, Z is a lower alkyl group as defined above, a halogen, a group  $\text{OR}^1$ , or a group  $\text{COOR}^1$  where  $R^1$  has the meaning defined above, m is 1, 2, or 3, n is 1, 2, or 3, and p is 0, 1, or 2.

2. A compound of formula I wherein the group R is a methyl or ethyl group, the group Y is a group  $\text{COOR}$  where R is defined above, and where p is 0.
3. The compound of structure A, B, C, D, E, or F.
4. A pigment preparation which comprises a combination of at least one yellow or orange pigment and at least one compound of formula I.

5. A pigment preparation according to claim 2 wherein the yellow pigment is the compound of formula II.



6. An aqueous ink which comprises a combination of a yellow or orange pigment and at least one compound of formula I.
7. An ink according to claim 6 wherein the yellow pigment is the compound of formula II.



Application No: GB 9927547.1  
Claims searched: 1-7

Examiner: Stephen Quick  
Date of search: 17 April 2000

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.R):

Int Cl (Ed.7):

Other: Online: CAS ONLINE

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
	No documents of relevance found	

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|---|--|
| X Document indicating lack of novelty or inventive step   | A Document indicating technological background and/or state of the art.  |
| Y Document indicating lack of inventive step if combined with one or more other documents of same category. | P Document published on or after the declared priority date but before the filing date of this invention.          |
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